

Studies of the Processes operative in Solutions.—Parts II–V.

By H. E. ARMSTRONG, F.R.S., and others.

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V E 6250 Electrolysis an effect of association.

D 7050 The ionic association hypothesis.

7175 Title.

7255 The dissociation hypothesis criticised.]

II. *The Displacement of Chlorides from Solution by Alcohol and by Hydrogen Chloride.* By H. E. ARMSTRONG, F.R.S., J. V. EYRE, Ph.D., A. V. HUSSEY and W. P. PADDISON.

Although innumerable determinations of solubility have been placed on record, little has been done to elucidate the phenomena of what may be termed competitive dissolution. A comprehensive series of determinations of the solubility of chlorides in presence of hydrogen chloride made by Engel* led him to the conclusion that, up to a certain point, the hydride displaces the salt approximately equivalent by equivalent, the sum of the equivalents being practically constant; eventually, however, in every case, the chloride falls off in displacing power. Almost the only attempt to deal with the problem in a rational manner is that made by Nernst in 1888, who discussed the mutual influence which salts exercise on one another on the assumption that the gas laws are applicable to liquids and from the ionic dissociation standpoint. Having in mind the fact that, although neutral gases are without influence, a separation of ammonium chloride at once takes place if either hydrogen chloride or ammonia be introduced into a space in which these products of its dissociation are in equilibrium with the chloride, Nernst† advocated the view that the degree of dissociation of a dissolved salt—and therefore its solubility—will be diminished if a compound containing either of the ions of the salt be introduced into the solution. In support of this contention, results were put forward showing that the solubility of silver acetate is diminished and to about an equal extent by equivalent amounts of

* 'Ann. Chim. Phys.,' 1888, [6], vol. 13, p. 370.

† 'Zeits. Phys. Chem.,' 1889, vol. 4, p. 372.

the electrolytes sodium acetate and silver nitrate—which are supposed to undergo dissociation in solution to about equal extents; whilst acetic acid—which is supposed to exist in aqueous solution almost undissociated—has little if any influence. The subject was subsequently dealt with more fully from the same point of view by A. A. Noyes.*

The circumstance that “unionisable” (by hypothesis undissociated) neutral substances such as methylic and ethylic alcohol are powerful precipitants was ignored by Nernst and Noyes.

Unfortunately, the data which have been placed upon record (irrespective of difficulties arising from the irregularity of the curves which they afford) are seldom sufficient for the satisfactory discussion of the problem of competitive solubility. In but few cases has the influence of one substance on another been determined in a graduated manner, saturated solutions alone having been dealt with by most observers.

In making the experiments to be referred to in this communication, alcohol and hydrogen chloride were chosen as precipitants of a number of chlorides because the one may be regarded as a representative non-electrolyte and a weak dehydrant, the other as a representative electrolyte and moderately powerful dehydrant. The main object in view being to determine their relative “concentrating effects” in competition with that of the salts selected, *weight-normal* solutions were used throughout the inquiry—*i.e.*, solutions containing in 1000 grammes of water a known proportion of the substance whose effect was to be determined in competition with that of another.† By operating in this way, the effect was ascertained which the

* *Ibid.*, 1890, vol. 6, p. 491.

† The saturated solutions were prepared by vigorously stirring the solid salt with the solvent in a large test tube (21 cm. by 3 cm.) supported in a large water bath, either a rectangular tank provided with a glass front and back or a deep circular pan; the temperature was carefully maintained at 25° by means of a spiral toluene gas regulator, whilst both bath and solvent were constantly stirred by means of a motor. The saturated solution was withdrawn by means of a pipette provided with a graduated neck and stop-cock (comp. Lowry, ‘Chem. Soc. Trans.’ vol. 89, p. 1036).

The density of the alcohol used was d_{19}^{19} 0.79405; the alcoholic solutions were prepared by weighing.

In the actual experiments, while the solid was being stirred with the solvent, the dried, weighed pipette was kept in a cylinder standing in the bath. Usually stirring was interrupted at the end of an hour; then as soon as the liquid was clear a sample was withdrawn by means of the warmed pipette. By weighing the pipette full of solution, the quantity withdrawn as well as the density of the liquid was ascertained. A second sample was taken in like manner at the end of another hour. In most cases the samples were diluted to a known volume and titrated either with silver nitrate alone or (when hydrogen chloride was used) first with standardised alkali. In the case of potassium iodide, the contents of the pipette was washed into a tared, wide mouth, conical flask,

substances brought into competition exercised upon and within a given mass of water, the vehicle or medium within which the interchanges were effected being present in constant amount; emphasis is laid on this point, as the consideration is one which is commonly neglected, although probably it is the most important to bear in mind in dealing with mixed solutions.

Table I is given in illustration of the method followed in reducing the observations; the subsequent tables contain the actual data:—

Table I.—Solubility of Sodium Chloride.

Dilute alcohol at 25° C. [1000 grammes
of Water + 1 mol. Et(OH).]

Water at 25° C					
Sample.	A.	B.	Sample.	A.	B.
Density of saturated solution.	$d_{25}^{25} 1.2015$	1.2019	Density of saturated solution.	$d_{25}^{25} 1.1794$	1.1793
Weight of saturated solution	grammes. 12.0758	grammes. 12.0915	Weight of saturated solution	grammes. 11.8480	grammes. 11.8368
Weight of salt found	3.2057	3.2100	Weight of salt found	2.9340	2.9300
Weight of water present	8.8701	8.8815	Weight of water + alcohol	8.9140	8.9068
			Weight of alcohol present (calculated)	0.3920	0.3917
			Weight of water present	8.5220	8.5151
Calculated from above, 100 grammes of water dissolve	36.14 sodium chloride.	36.14 sodium chloride.	Taking the value 36.14 grammes		
			the salt saturates.....	grammes of water. 8.1184	8.1073
			the alcohol controls.....	0.4036	0.4078
			46 grammes alcohol control	47.36	47.81
			1 mol. alcohol controls	2.63	2.66
				molecules of water	

which was heated in an air oven kept at about 110°—120°; it was found possible, in this way, to prevent the salt from creeping up the side of the vessel.

In reducing the observations, the weight of salt present was deducted from that of the solution; the weight of hydrogen chloride or alcohol in the remaining liquid was then calculated and deducted, the remainder was the amount of water present. The weight of water required to form a saturated solution with the amount of salt present was then calculated and deducted from that of the water present; assuming that the remaining water was associated with the precipitant, its molecular ratio to the latter was then calculated. The graphs are drawn to represent the variation of the presumed state of hydration of the precipitant with the variation in the amount of the precipitant; they therefore serve to picture the dehydrating activity of the precipitant.

Table II.—Sodium Chloride.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55.5 mols. of water.	Weight of saturated solution taken.	d_{25}^{25}	Weight of salt present.	Weight of alcohol present.			
—	grammes. A. 12.0758 B. 12.0915	1.2015 1.2019	grammes. 3.2057 3.2100	grammes. nil nil	grammes. 361.4 361.4	6.18 6.18	— —
$\frac{1}{4}$	A. 12.0192 B. 12.0020	1.1959 1.1957	3.1303 3.1275	0.1010 0.1009	356.2 356.5	6.09 6.09	3.20 3.04
$\frac{1}{2}$	A. 11.9553 B. 11.9516	1.1899 1.1896	3.0616 3.0616	0.1999 0.1998	352.2 352.3	6.02 6.02	2.84 2.80
1	A. 11.8480 B. 11.8368	1.1794 1.1793	2.9340 2.9300	0.3920 0.3917	344.3 344.1	5.88 5.88	2.63 2.66
2	A. 11.6426 B. 11.6462	1.1592 1.1593	2.7135 2.7109	0.7522 0.7528	331.8 331.3	5.67 5.66	2.27 2.31
5	A. 11.1688 B. 11.1656	1.1111 1.1115	2.1642 2.1602	1.6837 1.6839	295.6 295.0	5.05 5.04	2.02 2.04

Table III.—Potassium Chloride.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55.5 mols. of water.	Weight of saturated solution taken.	d_{25}^{25}	Weight of salt present.	Weight of alcohol present.			
—	grammes. A. 11.8600 B. 11.8561	1.1816 1.1813	grammes. 3.1676 3.1376	grammes. nil nil	grammes. 359.7 359.8	4.83 4.83	— —
$\frac{1}{4}$	A. 11.8196 B. 11.8060	1.1755 1.1754	3.0621 3.0611	0.0995 0.0994	353.7 354.0	4.75 4.75	3.73 3.45
$\frac{1}{2}$	A. 11.7386 B. 11.7363	1.1687 1.1689	2.9681 2.9681	0.1971 0.1971	346.2 346.3	4.64 4.64	4.2 4.1
1	A. 11.6073 B. 11.6178	1.1567 1.1568	2.8051 2.8138	0.3870 0.3871	333.3 334.3	4.47 4.49	4.08 3.93
2	A. 11.4002 B. 11.4046	1.1353 1.1357	2.5530 2.5604	0.7453 0.7451	315.1 316.1	4.23 4.24	3.44 3.37
5	A. 10.9018 B. 10.9012	1.0847 1.0847	1.8943 1.8977	1.6843 1.6836	258.6 259.2	3.47 3.48	3.12 3.10

Table IV.—Ammonium Chloride.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55.5 mols. of water.	Weight of saturated solution taken.	$d \frac{25}{25}$	Weight of salt present.	Weight of alcohol present.			
—	grammes. A. 10.8494 B. 10.8456	1.0808 1.0805	grammes. 3.0719 3.0719	grammes. nil nil	grammes. 395.0 395.2	7.39 7.39	— —
$\frac{1}{4}$	A. 10.8244 B. 10.8178	1.0779 1.0780	3.0468 3.0414	0.0884 0.0884	396.2 395.6	7.40 7.40	—0.64 —0.28
$\frac{1}{2}$	A. 10.8000 B. 10.7994	1.0753 1.0753	2.9862 2.9818	0.1756 0.1757	390.9 390.2	7.31 7.29	1.16 1.38
1	A. 10.7542 B. 10.7682	1.0706 1.0704	2.9051 2.9074	0.3452 0.3457	387.1 386.9	7.24 7.23	1.12 1.16
3	A. 10.5739 B. 10.5708	1.0528 1.0528	2.6007 2.6007	0.9668 0.9665	371.1 371.3	6.94 6.94	1.12 1.11
5	A. 10.4192 B. 10.4202	1.0377 1.0376	2.3537 2.3519	1.5082 1.5088	358.9 358.5	6.70 6.70	1.02 1.03

Table V.—Potassium Bromide.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55.5 mols. of water.	Weight of saturated solution.	Density of saturated solution, $d \frac{25}{25}$	Weight of salt present.	Weight of alcohol present.			
—	grammes. A. 13.8815 B. 13.8652	1.3830 1.3824	grammes. 5.6579 5.6548	grammes. nil nil	grammes. 688.0 688.7	5.78 5.79	— —
$\frac{1}{4}$	A. 13.7849 B. 13.7968	1.3725 1.3727	5.5609 5.5657	0.0935 0.0936	683.9 683.9	5.75 5.75	1.40 1.40
$\frac{1}{2}$	A. 13.6846 B. 13.6864	1.3634 1.3634	5.4111 5.4110	0.1860 0.1860	669.7 668.9	5.63 5.61	3.10 3.13
1	A. 13.4906 B. 13.5155	1.3445 1.3443	5.1818 5.1902	0.3654 0.3661	652.3 652.1	5.48 5.48	2.90 2.92
3	A. 12.8715 B. 12.8742	1.2815 1.2815	4.4026 4.4995	1.0269 1.0277	591.5 590.8	4.97 4.97	2.60 2.62
5	A. 12.3792 B. 12.3773	1.2318 1.2322	3.8232 3.8261	1.5999 1.5990	549.6 550.3	4.62 4.62	2.24 2.23

Table VI.—Potassium Iodide.

Displacement of Salt by addition of Ethyl Alcohol to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of alcohol per 55.5 mols. of water.	Weight of saturated solution.	Density of saturated solution, d_{25}^{25}	Weight of salt present.	Weight of alcohol present.			
—	grammes. A. 17.3318 B. 17.3565	1.7273 1.7268	grammes. — 10.3802	grammes. — nil	grammes. — 1487.9	— 8.96	— —
$\frac{1}{4}$	A. 17.2382 B. 17.2387	1.7157 1.7154	10.2440 10.2440	0.0795 0.0795	1481.5 1481.4	8.92 8.92	0.97 0.97
$\frac{1}{2}$	A. 17.1095 B. 17.1111	1.7036 1.7042	10.0920 10.0916	0.1578 0.1578	1471.2 1470.7	8.87 8.86	1.25 1.29
1	A. 16.8938 B. 16.9156	1.6833 1.6833	9.8122 —	0.3114 —	1449.3 —	8.73 —	1.47 —
3	A. 16.1388 B. 16.1244	1.6059 1.6063	8.8498 8.8535	0.8839 0.8817	1381.6 1385.7	8.32 8.33	1.32 1.27
5	A. 15.4879 B. 15.4940	1.5425 1.5420	8.0694 8.0690	1.3872 1.3885	1337.9 1336.6	8.06 8.06	1.12 1.13

Table VII.—Ammonium Chloride.

Displacement of Salt by addition of HCl to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt dissolved in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of hydrogen chloride per 55.5 mols. of water.	Weight of saturated solution used.	d_{25}^{25}	Weight of salt present.	Weight of HCl present.			
—	grammes. A. 21.5398 B. 21.5380	1.0797 1.0800	grammes. 6.1154 6.1154	grammes. — —	grammes. 396.48 396.52	7.41 7.41	— —
$\frac{1}{4}$	A. 21.5674 B. 21.5276	1.0810 1.0790	5.949 5.970	0.1446 0.1437	385.1 384.7	7.19 7.18	6.33 6.61
$\frac{1}{2}$	21.5816	1.0815	5.7346	0.2835	368.48	6.88	7.85
1	A. 21.6044 B. 21.6020	1.0827 1.0827	5.3531 5.3435	0.5783 0.5768	341.5 340.7	6.38 6.37	} 7.75
5	21.9396	1.0992	2.4890	3.0255	174.24	3.25	

Table VIII.—Sodium Chloride.

Displacement of Salt by addition of HCl to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of hydrogen chloride per 55·5 mols. of water.	Weight of saturated solution used.	$\Delta \frac{25}{25}$	Weight of salt present.	Weight of HCl present.			
—	grammes. A. 23·9584 B. 23·9810	1·2012 1·2018	grammes. 6·3570 6·3760	grammes. — —	grammes. 362·15 362·33	6·19 6·19	— —
$\frac{1}{4}$	A. 23·8920 B. 23·8862	1·1972 1·1970	6·0396 6·0253	0·153 0·154	341·2 340·2	5·93 5·92	12·559 12·601
$\frac{1}{2}$	23·7810	1·1915	5·8076	0·3175	328·93	5·62	10·19
1	A. 23·5816 B. 23·6174	1·1814 1·1822	5·2600 5·2674	0·6385 0·6408	297·5 297·4	5·08 5·08	} 9·91
5	A. 22·4010 B. 22·4218	1·1241 1·1238	1·5841 1·5776	3·2471 3·2525	90·16 89·61	1·54 1·53	

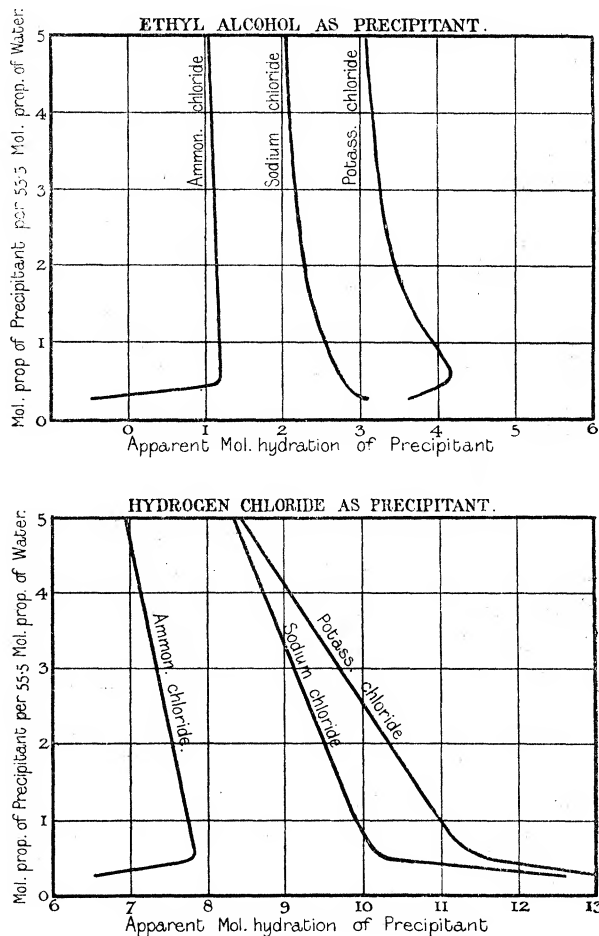
Table IX.—Potassium Chloride.

Displacement of Salt by addition of HCl to 1000 grammes of Water at 25° C.

Precipitant.	Saturated solution.				Weight of salt dissolved in 1000 grammes of water.	Molecular proportion of salt in 1000 grammes of water.	Apparent molecular hydration of precipitant.
Molecular proportion of hydrogen chloride per 55·5 mols. of water.	Weight of saturated solution used.	$\Delta \frac{25}{25}$	Weight of salt present.	Weight of HCl present.			
—	grammes. A. 23·5746 B. 23·5952	1·1810 1·1811	grammes. 6·2297 6·2407	grammes. — —	grammes. 360·83 359·60	4·84 4·82	— —
$\frac{1}{4}$	A. 23·4750 B. 23·4370	1·1766 1·1764	5·907 5·899	0·159 0·157	338·6 339·33	4·54 4·548	12·99 13·02
$\frac{1}{2}$	23·3786	1·1742	5·6321	0·0770	323·15	4·33	11·42
1	A. 23·1776 B. 23·1592	1·1617 1·1611	5·0551 5·0350	0·6397 0·6485	289·2 288·1	3·87 3·86	} 11·03
3	A. 22·5708 B. 22·5800	1·1320 1·1326	3·023 3·040	1·9218 1·9206	171·51 172·50	2·29 2·31	
5	A. 22·3344 B. 22·3244	1·1184 1·1184	1·5134 1·5477	3·2392 3·2169	86·07 88·14	1·02 1·18	} 8·42

If the apparent dehydrating power of the precipitant be taken as the measure of its activity in competition with the dissolved salt, it will be obvious, on reference to Diagram 1 (below), in the first place, that although alcohol is less active than hydrogen chloride, the same kind of influence is exercised by both precipitants, as the two sets of graphs correspond in most respects.

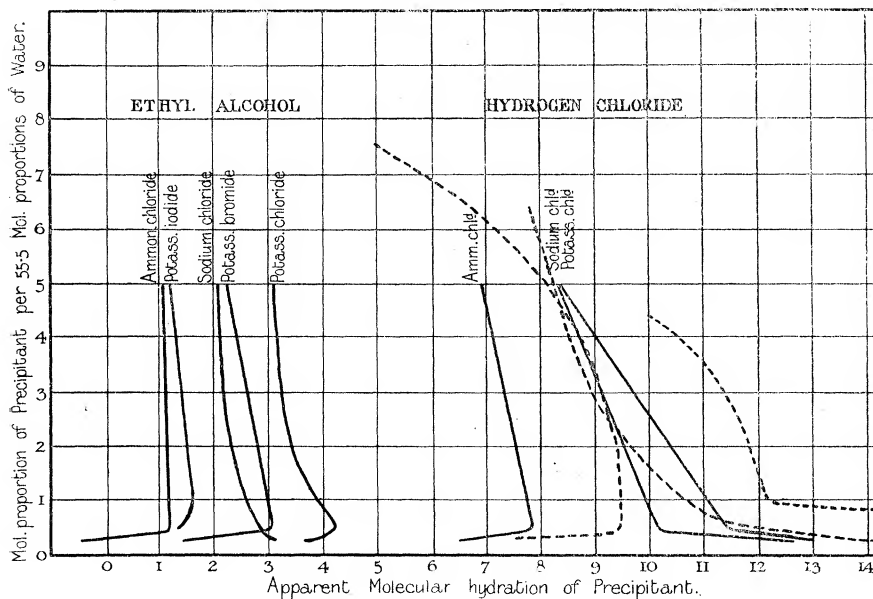
DIAGRAM 1.



It is important to consider Engel's results, and especially his conclusions, in connection with our determinations; as his observations were made at 0° they afford data for a comparison of the effects produced at 0° and 25° . Engel did not adequately take into account the proportion of water present, but assumed that the phenomena would be the same if considered with reference

to a constant amount of water;* when his observations are recalculated from our point of view (Table I) and the results are expressed by graphs, it is obvious that they correspond very closely with our own (Diagram 2).

DIAGRAM 2.



The graphs afford a most interesting picture of the state of the salts in solution at various stages. As the precipitant has the largest effect when present in least amount, it is clear that the condition of the salts in highly concentrated solutions is peculiar and different from that which they assume in presence of a considerable proportion of the precipitant: sodium and potassium chlorides both exist in an eminently precipitable form in the

* His statement on this point is as follows :—

6. Tant que le chlorure est précipité équivalent à équivalent par l'acide chlorhydrique, la quantité d'eau contenue dans un même volume de la solution du chlorure en présence de quantités variables d'acide est sensiblement constante. Il en résulte que le phénomène reste le même si l'on rapporte à un même poids d'eau la quantité de chlorure en solution en présence de quantités variables d'acide chlorhydrique.

7. L'acide chlorhydrique n'agit pas en fixant de l'eau et empêchant ainsi celle-ci d'agir comme dissolvant sur le chlorure. La quantité d'eau laissée libre par la précipitation d'un équivalent du sel varie, en effet, dans chaque cas, et, par suite, l'acide chlorhydrique s'opposerait à la dissolution de chaque chlorure en s'unissant lui-même à une quantité d'eau variable dans chaque cas et sensiblement égale à celle qu'exige, pour se dissoudre, un équivalent du chlorure considéré.

8. Enfin, l'eau qui se combine avec l'acide chlorhydrique et l'eau de cristallisation du chlorure semblent intervenir comme dissolvant, au même titre que le reste de l'eau,

concentrated solutions, water being held by them far less firmly than it is subsequently; ammonium chloride, on the other hand, is present in a form in which at first it is more soluble in the mixed solvent than in water.

As ammonium chloride is readily volatilised and, when vaporised, has a density corresponding to the formula NH_4Cl , it may be assumed that it enters into and exists in solution at least largely in the monadic form; but in concentrated solutions, in which, probably, there is not sufficient water to hydrate all the molecules, a considerable proportion of the monads are unhydrated and capable of combining with substances such as hydrogen chloride and alcohol. As the amount of precipitant is increased, the amount of salt in solution is diminished and a proportion is soon reached which permits of the hydration of most, if not all, of the salt molecules. Ere this stage is reached, however, the proportion of hydrogen chloride molecules present becomes sufficiently large once more to exert a solvent action on the salt, which, in consequence, is thrown out of solution in a diminishing proportion.

It can scarcely be doubted that the easily precipitable form of potassium and sodium chlorides is a complex, polymerised molecule, closely related, perhaps, to the solid form: in fact, the solution may be regarded as saturated

puisque le phénomène est le même pour les chlorures anhydres et pour les chlorures qui cristallisent avec de l'eau de cristallisation.

Engel's data for ammonium chloride are given by way of example in the following table, together with (in the last two columns) the corrected values we have calculated from them on the assumption that water is present in constant amount throughout.

Quantité de chlorure d'ammonium dans 10 c.c. de solution saturée en présence de quantités variables d'acide chlorhydrique.

—	NH_4Cl .	HCl .	Comme des équivalents.	Densité.	Eau.	Calculated from data given in table—	
						Molecular proportion of HCl in 1000 grammes of water.	Molecular hydrate value.
I	46.125	0	46.125	1.076	8.29	grammes.	—
II	43.6	2.9	46.5	1.069	8.25	0.351	7.49
III	41.0	5.5	46.5	1.070	8.31	0.661	9.477
IV	39.15	7.85	47.0	1.071	8.33	0.942	9.05
V	36.45	10.85	47.30	1.093	8.39	1.29	9.43
VI	27.37	21.4	48.7	1.078	8.53	2.50	9.29
VII	10.875	53.0	63.875	1.106	8.54	6.21	6.88
VIII	8.8	61.0	69.8	1.114	8.12	7.51	4.96

with the solid with which it is in equilibrium. Comparison of the observations at 0° and 25° seems to show that this "solid form" persists in presence of a larger proportion of the precipitant at 0° than it does at 25° , at least a molecular proportion of hydrogen chloride being required to destroy it at 0° and only about half as much at 25° . Moreover, to judge from the shortness of the horizontal branches of the sodium and potassium chloride graphs at 0° in comparison with those at 25° , it would seem that at the higher temperature these chlorides are also to some extent present as unhydrated monads soluble in the precipitant.

In the case of ammonium chloride, the increased solubility is noticeable at 0° at a somewhat "higher level" than at 25° , probably because the more soluble chloride $\text{NH}_4\text{Cl} : \text{ClH}$ is more stable at the lower temperature.

It will be seen that in the case of ammonium and potassium chloride the 0° graphs curve more and more to the left as the concentration of the hydrogen chloride is increased; no such marked trend is noticeable at 25° . It is to be supposed that the difference arises from the instability of the double chlorides at the higher temperature in competition with water. The fact that the alcohol graphs resemble the 25° hydrogen chloride graphs affords support to this view, as it is to be expected that alcohol would have but little chance in competition with water.

From the ionic dissociation point of view, dissociation should be repressed as the amount of hydrogen chloride is increased: therefore, instead of increasing, the solubility should diminish proportionally as the concentration of the hydrogen chloride is increased.

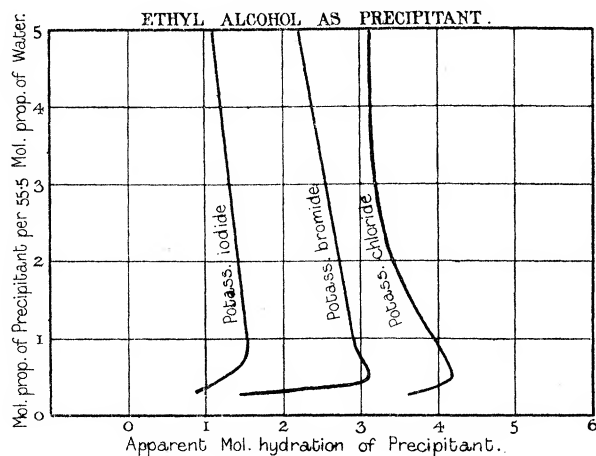
It will be observed that the behaviour of potassium bromide and iodide in presence of alcohol is similar to that of the chloride and that the greater the molecular solubility of the salt the more closely it approximates to ammonium chloride; probably the proportion of monads in the concentrated solution is larger in the case of the more soluble salt, which also has the lower melting point (Diagram 3).*

Except, perhaps, in the case of ammonium chloride, the greater proportionate solubility of the salts in regions represented by the upper portion of the diagram, as well as the lower state of hydration of the precipitant which is indicated by the backward slope of the graphs, can only in part be ascribed to the formation of a soluble compound with the precipitant; probably it is mainly due to the production of the more soluble monads in increasing

* It is perhaps appropriately suggested here that probably the great increase in molecular solubility of ammonium chloride (from about 6 to 13.5 proportions per 1000 grammes of water) between 0° and 100° is to be correlated with the low melting point of the salt.

proportion as the number of interposed molecules of the precipitant is increased. The same kind of effect is reciprocally exercised by two salts such as potassium and sodium chloride, a saturated solution containing per 1000 molecules of water of the former 88 and of the latter 111 molecular proportions, whilst a solution saturated with both salts contains 39 of the former to 89 of the latter : or, in sum, 128, an excess of $128 - 111 = 17$ monadic proportions over the number contained in a saturated solution of the more soluble salt. The monads of the two salts evidently interfere with one another's freedom of combination : consequently, the mixed solution contains, in the aggregate, a greater number of molecules than can coexist in the

DIAGRAM 3.



solution of the more soluble salt ; evidence in support of this view is to be found in the fact that the solution of the mixed salt has a lower vapour pressure (16.84 mm.) than has the solution of sodium chloride (17.7) or that of potassium chloride (19.2). In the mixed solution, at 25° , the more soluble sodium chloride is present in a proportion somewhat larger than that corresponding to its solubility in comparison with the solubility of potassium chloride ; evidently, therefore, it is able to compete somewhat more successfully for the water. This preponderance of the more soluble salt is even more obvious in cases in which the competition is with a salt which is but moderately soluble and which, therefore, presumably has but a slight hold upon the water—for example, whereas potassium chloride and sulphate are present in their saturated solutions in the relative molecular proportions of 88 to 12, a solution saturated with both salts contains to 84 of the former only 1.5 molecular proportions of the latter, and its vapour pressure (19 mm.) is

but slightly less than that of chloride alone (19·2). The solubility of sodium chloride in the presence of potassium chloride, it is well known, diminishes slightly between 0° and 100°; this is probably due to the diminution in its affinity for water as the temperature rises and the concomitant increase in the tendency to reform complex molecules—the decomposition of which at lower temperatures must be regarded as determined largely by the affinity of water for the monads. At 100° potassium and sodium chlorides are almost equally soluble (4·4 : 4·6 molecular proportions), the former having the advantage—probably because it can hold water more firmly.

The distinction between monadic and polymerised molecules has been almost left out of account by those who have attempted to apply the ionic dissociation hypothesis to the discussion of solubility. It is clearly necessary, however, to acknowledge the existence in solutions of a great variety of molecular conditions simultaneously: of monadic and polymerised molecules both in the anhydrous and hydrated states and, in some cases, of compounds formed by the association of the admixed solutes; and also to recognise that the solvent itself as well as the dissolved substances is in a state of continued flux. The interplay of these conflicting and competing elements is sufficient, probably, to account for all the varied phenomena afforded by solutions without the introduction of hypothetical considerations based on the presumed occurrence of dissociation into independent ions. And even if, on other grounds, it were necessary to postulate the occurrence of ionic dissociation in solution, the phenomena are clearly of so complicated a character that it is impossible to apply such an interpretation without introducing the many other considerations which obviously demand attention. The variables are so numerous that it may be doubted whether it will ever be possible to develop any simple treatment of solutions.

III. *The Sacroclastic Action of Nitric Acid as influenced by Nitrates.* By R. WHYMPER, Salters' Company's Research Fellow, City and Guilds of London Institute, Central Technical College.

The experiments carried out by R. J. Caldwell on the hydrolysis of cane sugar by chlorhydric acid in presence of various chlorides, described in the first of these studies,* have afforded a means of judging of the extent to which such salts exercise a concentrating effect and of determining the average degree of hydration of the chlorides in solution. In the present

* 'Roy. Soc. Proc.,' 1906, A, vol. 78, p. 272.

communication it will be shown that the method is equally applicable to nitrates and that these are nearly as fully hydrated in solution as are the corresponding chlorides—a conclusion of some interest, as nitrates are not usually credited with any considerable dehydrating power.

My observations have been made with the apparatus* which was used by Caldwell and in the manner described by him; throughout the enquiry I have also enjoyed the advantage of his experience and have to thank him for the advice which he has given me.

The salts examined were recrystallised until neutral, the ammonium nitrate from alcohol. The acid used in preparing the solutions was approximately twice normal; it was titrated against calcite and also against a solution of baryta standardised by another worker.

The solution to be examined was filtered into the polarimeter tube at as near to 25° as possible and the tube was then placed in position in the heated jacket attached to the instrument. To give time for the liquid to acquire the temperature of the thermostat, it was found to be advisable to wait before taking the initial reading until about 20 minutes later, when the rotatory power was about 10° to 11° ; by operating in this manner, the error due to initial disturbances is avoided. Mean time readings were taken at 30, 35 100 minutes after the first: a final reading was taken to determine the end point at least 24 hours later, when the action was practically at an end. Each reading reported represents the mean of five readings taken at minute and half minute intervals on either side of the mean time.

The results obtained in two complete experiments entirely representative of the series are recorded in Tables I and II. It will be noticed that the 30-minutes values are both high: this is almost uniformly the case and appears to be due to the fact that the eye was less sensitive just after coming into the dark room than it was subsequently. The thermometers attached to the jacket were watched throughout the experiment and it was usually possible to correlate marked changes in the value of the constant with any unusual variation of the temperature. An illustration of this fact is given in Table I: it will be seen that the value of K at 35 minutes is given as 12 units above the mean value; a fall in temperature of about $0^{\circ}.1$ was noticed when the reading was taken at this time.

* To adjust the rate of flow of the water through the jacket of the polarimeter tube, the water was passed through a tube in which a glass rod, of nearly the same diameter, could be moved up and down; this tube was provided with inlet and exit tubes and the water passed through the interval between the rod and the main tube. By shifting the rod, the rate of flow of the water could be adjusted far more delicately than by means of the ordinary screw clip arrangement.

Table I.— $\frac{1}{2}$ gramme-molecule of Cane Sugar + 1 gramme-molecule of HNO_3
+ 1 Gramme-molecule of LiNO_3 + 1000 grammes of H_2O + $13\text{H}_2\text{O}$.

t .	α_{D}^{25} .	$a-x$.	$K\left(\frac{10^5}{t} \log \frac{a}{a-x}\right)$.
0	9.433	14.766	—
30	5.35	10.683	468
35	4.733	10.066	475
40	4.333	9.666	460
45	3.8	9.133	463
50	3.333	8.666	463
55	2.883	8.216	463
60	2.417	7.75	467
65	2.033	7.366	465
70	1.667	7.0	463
75	1.333	6.666	461
80	0.967	6.3	462
85	0.65	5.983	462
90	0.333	5.666	462
95	0.017	5.35	464
100	-0.2	5.133	459
∞	-5.333		
			Mean 463

Table II.— $\frac{1}{2}$ gramme-molecule of Cane Sugar + 1 gramme-molecule of HNO_3
+ 1 gramme-molecule of AgNO_3 + 1000 grammes of Water.

t .	α_{D}^{25} .	$a-x$.	$K\left(\frac{10^5}{t} \log \frac{a}{a-x}\right)$.
0	11.1	17.767	
30	5.533	12.2	544
35	4.85	11.517	538
40	4.233	10.9	531
45	3.567	10.234	533
50	3.013	9.68	528
55	2.367	9.034	535
60	1.883	8.55	530
65	1.333	8.0	533
70	0.85	7.517	534
75	0.4	7.067	534
80	0.033	6.7	530
85	-0.367	6.3	530
90	-0.683	5.984	525
95	-1.033	5.634	525
100	-1.4	5.267	528
∞	-6.667		
			Mean 531

The data relating to the various salts which were studied are collected in Table III.

Table III.— $\frac{1}{2}$ gramme-molecule of Cane Sugar + 1 gramme-molecule of HNO_3 + 1 gramme-molecule of Salt + 1000 grammes of Water + X gramme-molecules of Water.

Salt.	Volume of solution.	$K \left(\frac{10^5}{t} \log \frac{a}{a-x} \right)$.	X (gramme- molecules).	K.	Average hydrate.
Sugar alone ...	c.c. 1136.4 1136.6 1137.1	463 467 466			
AgNO_3	1173.3	Mean 465 531	20 H_2O 9 H_2O 6 H_2O 5 H_2O	339 429 459 { 465 466	5 H_2O .
NH_4NO_3	1167.9	570	10 H_2O 7 H_2O	444 { 466 466	7 H_2O .
KNO_3	1180.1	566	10 H_2O 8 H_2O	453 { 462 465	8 H_2O .
NaNO_3	1172.1	607	20 H_2O 12 H_2O 11 H_2O	373 444 { 464 466	11 H_2O .
LiNO_3	1179.3	578	7 H_2O 10 H_2O 11.5 H_2O 13 H_2O 15 H_2O	488 478 477 463 432	13 H_2O .
$\text{Sr}(\text{NO}_3)_2$	1197.9	733	23 H_2O 20 H_2O 18 H_2O	420 443 { 463 463	18 H_2O .

The results call for little remark, as the hydration values arrived at, given in the last column of the table, seem to be entirely rational. It is difficult to avoid the conclusion that they dispose of the contention that nitrates exist in solution unhydrated.

IV. *The Hydrolysis of Methyl Acetate in Presence of Salts.* By

H. E. ARMSTRONG, F.R.S., and J. A. WATSON.

In principle, the method developed in the first of these studies of determining the average "concentrating effect" of a salt on the activity of an acid hydrolyst is applicable to all cases of hydrolysis other than those

induced by enzymes; moreover, the results obtained with chlorides and nitrates with cane sugar are so entirely rational that there can be little doubt that it is valid generally as a means of determining the average degree of hydration of a salt in solution. But as the substances in a solution share the solvent and are in competition, it is to be expected that hydration values will be found to vary from case to case and that it will not always be possible to approximate to the true hydrating effect of a salt: indeed, cases are known in which salts apparently retard hydrolysis.

To determine the limitations of the method, therefore, it is necessary to investigate the behaviour of hydrolytes other than cane sugar. That chosen for the experiments referred to in this account was the ethereal salt *methylic acetate*, $\text{CH}_3\text{CO.OCH}_3$. This substance is entirely different in constitution from cane sugar and is present in solution, presumably, in the form of simple molecules which are hydrated to but a very slight extent, whilst cane sugar doubtless exists in solution more or less in the form of associated complex molecules and in a moderately hydrated condition—perhaps as a “hexhydrate” at least. Presumably, therefore, the system consisting of water, chlorhydric acid and cane sugar contains less “free water” than the equivalent system in which methylic acetate takes the place of sugar: a salt dissolved in the latter system should, at least in concentrated solutions, therefore have a greater chance of becoming hydrated than it would have if dissolved in the former. From this point of view it was to be expected that the hydration values deduced with the aid of methylic acetate, if not coincident with those determined by means of cane sugar, would be higher; as a matter of fact, lower values are obtained.

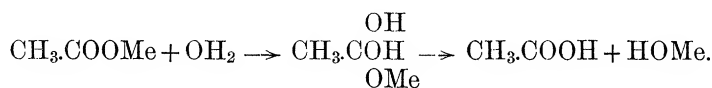
The average degree of molecular hydration arrived at with the aid of the two hydrolytes is as follows:—

—	Hydrolysis by chlorhydric acid.		—	Hydrolysis by nitric acid.	
	Sugar.	Acetate.		Sugar.	Acetate.
—	—	—	Silver nitrate ...	5	
Ammonium chloride ...	10	5	Ammonium „ ...	7	—2
Potassium „ ...	10	8	Potassium „ ...	8	1
Sodium „ ...	13	10	Sodium „ ...	11	3
Lithium „ ...	—	—	Lithium „ ...	13	
Barium „ ...	19	18	Barium „ ...		
Strontium „ ...	—	—	Strontium „ ...	18	+5 (?)
Calcium „ ...	22	20	Calcium „ ...	—	7

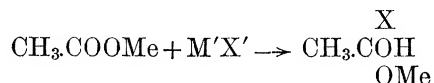
The results are very remarkable—evidently some special influence comes

into play, particularly in the case of the nitrates. It is not difficult to diagnose the character of this influence.

It has been shown by Arrhenius* and by Spohr† that chlorides and nitrates, but not sulphates, exert a slight retarding effect on the hydrolysis of ethylic acetate by alkali: therefore it is probable that a similar retarding influence comes into play when hydrolysis is effected by an acid and that this to some extent masks and counteracts the proper accelerating effect of the salt. Probably the effective hydrolyst is the hydrated acid: assuming, however, for the sake of simplicity, that water acts alone, the hydrolysis of the ethereal salt doubtless involves the association of the two molecules and subsequent partition of the complex into acid and alcohol, thus—



A simple explanation is afforded of the interference of a salt and of the diminished acceleration or retardation observed in the case of methylic acetate, if it be assumed that the salts (M'X') also enter into association with the ethereal salt—



and that consequently they hinder to some extent the association of ethereal salt and hydrolyst.‡ The keto-group, CO, is so generally admitted to be unsaturated and capable of combining with compounds of the form R'X' that such an explanation cannot be regarded as otherwise than simple and rational. We are not aware, however, that it has been suspected up to the present time that nitrates are peculiarly active in thus combining.

Results such as we have described are altogether irreconcilable with the tenets of those who accept the doctrine of ionic dissociation. They serve, however, to explain the results obtained on hydrolysing ethereal salts with alkali in presence of metallic salts, and we venture to think that it is no

* 'Zeit. Phys. Chem.,' vol. 1, p. 1107. According to Arrhenius, the effect on the rate of hydrolysis by sodic hydrate of the corresponding salts is greater than that exercised by the potassium salts on the activity of potassic hydrate. Potassium iodide has a greater influence than the bromide, which in turn is more active than the chloride. Arrhenius speaks of the retardation as a perturbation of the second order, due to forces the true nature of which will not be easily determined.

† *Ibid.*, vol. 2, p. 194.

‡ In the case of hydrolysis by alkali, the experiments have been made with quite dilute solutions, between limits within which concentration has but little influence, so that the concentrating effect of the salt cannot well become apparent merely as a diminished acceleration and there is consequently an actual retardation.

longer necessary to associate any element of mystery with such hydrolytic phenomena; the long recognised conventional articles of belief of the chemist afford a sufficient and satisfactory explanation of the observed departures from uniformity.

The hydrolysis of methylic acetate by acids was first investigated systematically by Ostwald in 1883 and developed by him into a method of appraising the relative activity of acids. Trey, at Ostwald's instigation, shortly afterwards studied the effect of several neutral salts on the action of the corresponding acids and showed that they exercised an accelerating influence; as Trey's and all subsequent experiments, however, were made with volume-normal solutions, it has remained uncertain to the present time whether or to what extent the increased activity of the acid is due to the mere displacement of water by the salt. It was, therefore, desirable to institute experiments in which the water was no longer a variable, so that the specific influence of the salt might be ascertained and its degree of hydration determined, following the plan developed in Part I of these studies.

The solutions we have used contained, as a rule, 1000 grammes of water, $\frac{1}{2}$ gramme-molecular proportion of methylic acetate and 1 gramme-molecular proportion of hydrogen chloride or nitric acid; when a salt was added, 1 gramme-molecular proportion was always used.

In carrying out the experiments, 100 c.c. of twice weight-normal acid (chlorhydric or nitric) was introduced into a Jena flask and when the temperature of the liquid was 25° a like quantity of a weight-normal solution of methylic acetate, also at 25° , was quickly added; the two solutions having been mixed, 10 c.c. were promptly withdrawn and run into 10 c.c. of a solution of twice normal sodic acetate, the time being noted; the flask containing the main bulk of the solution was forthwith placed in the thermostat, which was carefully kept at 25° . Samples were withdrawn every 10 minutes up to two hours from the commencement of the experiment. The end point was determined the next morning. An important improvement was effected by using the sodic acetate to check the action of the strong acid. The titrations were made with $N/5$ baryta, using phenolphthalein as indicator.

When salts were added, the weighed quantity of salt was dissolved in the acid solution before the solution of methylic acetate was run in. In some cases, in order to dissolve the necessary amount of salt, 50 c.c. of water were added to the acid and the solution of methylic acetate was made of double strength. The first reading was taken only after 30 minutes from the commencement of the experiment.

Two complete series of observations are given in Table I.

Table I.

Composition of Solution—

14.92 grammes KCl.

100 c.c. 2N/HCl.

100 c.c. N/MeAc.

KCl.8H₂O—

14.92 grammes KCl.

100 c.c. HCl.

100 c.c. MeAc.

28.82 c.c. water.

Time.	Titration.	$a-x$.	$\frac{10^5}{t} \log \frac{a}{a-x}$.	Time.	Titration.	$a-x$.	$\frac{10^5}{t} \log \frac{a}{a-x}$.
	c.c.				c.c.		
0	52.3	23.3	—	0	45.9	21.3	—
30	57.4	18.2	357*	30	49.9	17.3	301
40	58.5	17.1	336	40	51.2	16.0	310
50	59.7	15.9	332	50	52.2	15.0	304
60	60.9	14.7	333	60	53.25	13.95	306
70	62.2	13.4	342	70	54.2	13.0	306
80	63.1	12.5	338	80	55.05	12.15	305
90	64.1	11.5	340	90	55.9	11.3	305
100	65.05	10.55	344	100	56.7	10.5	307
110	65.7	9.9	337	110	57.4	9.8	306
End point	75.6	Mean...	338	End point	67.2	Mean...	305

* The values entered in *italics* were neglected.

The following (Table II) are the values of the velocity constant obtained with acetate alone or with salt present in the solution and those on which the determinations of the hydration values are based.

It will be noticed that the values are not as accordant as those determined with the aid of the polarimeter, but this was only to be expected, as the possibility of error is so much greater, owing to the numerous measurements to be made with pipettes and the difficulty of taking samples at exactly the right times, as well as of checking the action; moreover, titration is not nearly so accurate a process as the estimation of optical activity.

Table II.

Me \bar{A} + HCl.		+ KCl.	KCl.8H ₂ O.		+ NaCl.	NaCl.10H ₂ O.		+ NH ₄ Cl.	NH ₄ Cl.5H ₂ O.	
303	291	357	301	318	385	299	292	313	301	310
296	300	336	310	316	359	300	298	276	290	300
303	300	332	304	294	341	305	313	314	307	301
290	312	333	306	303	361	316	302	321	322	305
307	308	342	306	295	360	309	299	316	307	310
304	310	338	305	301	361	302	303	325	310	309
301	303	340	305	297	361	314	298	329	310	—
—	305	344	307	303	360	—	301	—	316	—
—	308	337	306	—	—	—	301	—	—	—
302	304	338	305	303	360	303	301	320	306	306
303			304			302			306	

BaCl ₂ .18H ₂ O.			+ CaCl ₂ .	CaCl ₂ .20H ₂ O.	Me \bar{A} + HNO ₃ .		+ KNO ₃ .	KNO ₃ .H ₂ O.	+ NaNO ₃ .
304	297	307	420	292	281	234	265	289	268
311	312	316	418	304	298	270	282	284	279
318	311	306	428	304	266	278	284	273	290
314	307	311	421	305	284	283	284	274	294
314	291	307	430	302	276	279	280	275	290
301	310	313	429	299	272	279	285	269	290
298	304	309	—	299	278	272	286	277	284
—	295	302	—	299	277	282	—	276	—
—	307	—	—	—	—	282	—	—	—
309	304	308	424	300	278	278	283	277	290
307					278			277	

NaNO ₃ .3H ₂ O.	NH ₄ NO ₃ .	NH ₄ NO ₃ -2H ₂ O.	+ LiNO ₃ .	Ca (NO ₂) ₂ .7H ₂ O.
291	254	242	257	260
274	245	250	267	277
270	256	273	276	274
272	274	279	278	272
273	261	278	277	274
277	266	269	280	277
272	268	273	277	276
				274
				278
273	263	275	278	275

The results obtained are summarised in the following Table III:—

Table III.—Rate of Hydrolysis of Methylic Acetate by Chlorhydric and Nitric Acids in Solutions of different Compositions.

Composition of solution.	$\frac{10^5}{t} \log \frac{a}{a-x}$	Amount of water added.
		gramme-molecules.
0.991 N/HCl + N/MeAc	303	
+ N/2 MeAc	294	
	294	
+ N/4 MeAc	282	
+ N/2 MeAc + N/2MeOH	292	
	293	
	294	
+ N/2CH ₃ CO ₂ H	311	
	316	
N/HCl + N/2 MeAc	302	
	304	
+ KCl, 1 gramme-molecule	338	
	290	9
	305	8
	303	
+ NaCl, 1 gramme-molecule.....	360	
	287	12
	303	
	301	10
+ NH ₄ Cl, 1 gramme-molecule	320	
	306	5
	306	
+ CaCl ₂ , 1 gramme-molecule	424	
	300	20
+ BaCl ₂ , 1 gramme-molecule	320	10
	309	18
	304	
	308	
N/HNO ₃ + N/2 MeAc	278	
	278	
+ KNO ₃ , 1 gramme-molecule	283	
	277	1
+ NaNO ₃ , 1 gramme-molecule.....	290	
	273	3
+ LiNO ₃ , 1 gramme-molecule	278	
+ NH ₄ NO ₃ , 1 gramme-molecule	263	
Less 2 gramme-molecules of water	275	-2

Although, as hydrolysis proceeds, both methylic alcohol and acetic acid are formed and accumulate in solution, the results afford no evidence that they influence the rate of change. The effect of these substances when added in advance is different, methylic alcohol being apparently without action, whilst acetic acid has a distinct accelerating influence*—as it has in the hydrolysis of cane sugar. That the alcohol has no influence is

* It has practically no hydrolytic effect *per se* during the time occupied in carrying out an experiment.

somewhat surprising in view of the fact that ethylic alcohol retards the hydrolysis of cane sugar to a not inconsiderable extent; this difference between the two cases is, perhaps, significant and deserving of further study. Apparently, the concentrating effect which the methylic alcohol may be supposed to exercise is just balanced by the extent to which it acts in neutralising acid; on the other hand, it would seem that the acid alcoholate is not much less active than the acid hydrate, although in the case of cane sugar it is relatively ineffective. The effect of increasing the concentration of the ethereal salt appears to be very similar to that observed in the case of cane sugar.

It is proposed to extend the experiments to other ethereal salts.

V. *The Discrimination of Hydrates in Solution.* By H. E. ARMSTRONG, F.R.S., and R. J. CALDWELL, B.Sc., Leathersellers' Company's Research Fellow, City and Guilds of London Institute, Central Technical College.

There are many signs that the uncertainty which has so long attended the interpretation of the peculiarities manifest in solutions may be dispelled at no distant date and a common understanding arrived at, as the old belief in the existence of hydrates is once more coming to the front* and there is a growing tendency to admit that the phenomena are more complex than is commonly supposed.

Inasmuch as there are no arguments from the chemical side which either compel or even require belief in ions as independent entities and not a few incompatible with such an assumption, which support the view that association†—not dissociation—is the precedent of chemical interchange, physicists may well be challenged to reconsider the grounds on which they are led to suppose that ionic dissociation takes place in solution: the cogency of their arguments has been frequently questioned from the chemical side without the objections being met.

To state the case briefly: apart from the fact that it is irrational and inapplicable to compounds generally (only to electrolytes), three main lines of argument appear to militate directly against the assumptions postulated by the advocates of the ionic dissociation hypothesis.

1. The complex sugars and ethereal compounds generally are hydrolysed by all acids; and these latter differ only in the degree of activity which they

* Comp. Nernst, 'Zeits. phys. Chem.,' 1889, vol. 4, p. 372; 'Centralblatt,' 1900, vol. 2, p. 620.

† Comp. E. Fischer, 'Deut. chem. Ges. Ber.,' 1907, vol. 40, p. 495.

manifest towards the various hydrolytes. Enzymes, on the other hand, act selectively. The strength of the case which this argument affords is probably in no way realised by those who are not fully conversant with the phenomena. It is assumed by the ionic dissociation school that the action of acids is exercised by the free hydrogen ions and that the activity of the acid is proportional to the extent to which the acid is dissociated in solution into positive and negative ions. But as enzymes do not behave as electrolytes in solution, although extraordinarily active in comparison with acids, some other explanation must be found to account for their activity as hydrolysts. The proof that the enzyme enters into association with the hydrolyte appears to be complete* and as there is reason to believe that acids also combine transiently with ethereal compounds, there seems to be no reason why an explanation should be given of their action which is inapplicable to enzymes.

2. From the ionic dissociation standpoint, the dissociation of an acid into free ions should be repressed by a neutral salt containing the negative ion of the acid; consequently, when present together with the acid, as the salt is inert *per se*, the salt should diminish the activity of the acid: in point of fact, it increases it. As non-electrolytes sometimes exercise an accelerating influence similar to that of salts, although to a less extent, there is again no reason to attribute altogether special properties to electrolytes and to account for their activity by an explanation which cannot be applied to non-electrolytes.†

3. This same argument may be applied to the precipitation of salts from solution, as non-electrolytes are active as well as electrolytes.‡

* 'Roy. Soc. Proc.,' B, 1907, vol. 79, p. 360.

† An argument to the same effect may be based upon the fact that hydrogen chloride, calcium chloride and alcohol produce similar effects in altering the absorption spectrum of cobalt salts (Hartley, Royal Irish Academy, 1900, II, vol. 7, p. 253).

‡ In tracing the development of the theory of electrolytic dissociation, in a lecture which he gave at the Royal Institution on June 3, 1904 ('Proceedings of the Royal Institution,' vol. 17, p. 552), Arrhenius laid stress on the fact that in the case of permanganic acid and its various metallic salts, as well as in the case of the salts of pararosaniline with acids, the absorption spectrum does not vary from salt to salt except in intensity, whereas the spectrum of fluorescein is modified by the smallest chemical change of the molecule: he advances the explanation that the uniform behaviour of permanganates and of rosaniline salts is due to the fact that the spectra are all produced by the dissociated permanganate ion in the one case and by the rosaniline ion in the other. Those who have made use of this argument have paid little attention to what is known of the relation of colour to structure: it is well established, in the case of fluorescein, that the action of alkali extends beyond the formation of a salt and involves the formation of an isodynamic compound of entirely different structure and very differently coloured; no such change of structure is involved in the formation of the permanganates and of the ordinary rosaniline salts. In the case of rosaniline it is possible, by varying the proportions of acid, to produce salts of different structure, in which case the colour

The one respect in which electrolytes and non-electrolytes undoubtedly differ is in their affinity for water—which appears to enter into combination with the former in some particularly intimate manner; it is reasonable to suppose that their special behaviour towards an electric current is conditioned by this peculiarity. From this point of view, the study of the phenomena of hydration is of exceptional importance.

It appears to be now so widely admitted that hydrates are formed in solution that it is unnecessary to discuss the subject from the general point of view; the question to be decided is rather what particular hydrates are present. Passing over evidence such as has been adduced by Mendeleeff, Pickering, Hartley and others, the recent work of Harry C. Jones may be specially referred to, as he has brought forward a large amount of what purports to be new experimental evidence bearing on the determination of the extent to which salts are hydrated in solution.*

also varies. The argument from colour, far from supporting the dissociation hypothesis, in reality is opposed to it.

* The values which this observer arrives at are in many cases so remarkable that his methods appear to be more than open to doubt. Thus he considers that sodium, potassium and ammonium chlorides have little, if any, attraction for water and that the nitrates are even less hydrated than the corresponding chlorides. Magnesium and other sulphates give abnormal results; this salt “appears to form no hydrates in aqueous solution, notwithstanding that it crystallises with 7 molecules of water . . . it has considerable hydrating power, but this is masked by the large amount of polymerisation which the sulphates undergo.” As the concentration is increased, the degree of hydration of caustic soda falls to zero and then rises. And whilst ammonium hydroxide is regarded as being as highly hydrated as caustic soda and potash, the mineral acids are uniformly represented as anhydrous in dilute and hydrated in concentrated solutions.

The method adopted by Jones on which these conclusions are based involves, in principle, the assumption that the number of units—whether ions or molecules—in solution can be deduced directly from observations of the electrical conductivity; it also involves the assumption that this value can be deduced equally well from the depression of the freezing point even in concentrated solutions made on the volume-normal plan. In cases in which the two values differ, the difference is attributed to the formation of a hydrate and the magnitude of the difference is the basis on which the degree of hydration is calculated. Apart from the fact that the method involves both the acceptance of the ionic hypothesis and the application throughout of the 1.86 factor in calculating the theoretical depression of the freezing point, it is noteworthy that Jones also leaves out of account in his calculation the effect of hydration on the ionic mobilities and that no allowance is made for polymerisation effects.

Biltz (*Zeits. phys. Chem.*, 1902, vol. 40, p. 185), who recognises that the formation of hydrates in solution may be the cause of some of the abnormal properties of strong electrolytes, has endeavoured to support this view by the argument that as caesium nitrate—which he assumes is but slightly, if at all, hydrated in solution—depresses the freezing point in accordance with the Ostwald dilution law, it is to be regarded as behaving normally. The electric conductivity of such solutions is not that to be expected from the freezing point results, however; it therefore follows that conductivity cannot be taken as a true measure of the state of dissociation even in the case of salts which are

The method adopted in Parts I, III and IV of these studies is in principle independent of the assumptions made by those who accept the ionic hypothesis as a basis of calculation. Using cane sugar as hydrolyte, the average values arrived at in the case of a number of chlorides and nitrates appear to be such as are to be expected; the fact that somewhat lower values are obtained with the aid of methylic acetate can be accounted for without difficulty, as already pointed out. It was our intention to discuss our results in connection with the observations of previous workers, especially with reference to the influence of salts and certain non-electrolytes on the solubility of various gases; in this we have been somewhat anticipated by Philip, who, in a recent communication to the Chemical Society,* has developed the method of calculating the degree of hydration of a salt from existing data as to the influence of salts on the solubility of gases.

Although no attempt had been made previously to deduce hydration values from changes in solubility, Setschenow,† Tilden‡ and Rothmund§ had contemplated the possibility of explaining the diminution in solubility of non-electrolytes as a consequence of the diminution in the amount of free water by the fixation of water by the dissolved salts. Jahn,|| moreover, had foreseen the importance of referring the solubility to the weight of solvent used instead of to the volume of solution. Philip has only called attention to a few cases of close agreement—but it will be seen on reference to Table I, in which the results deduced from the various available observations are collected together, that the agreement is far from being close in many cases. In some cases, doubtless, the determination is affected by relatively large experimental errors, as, for example, Braun's determinations made with nitrogen; Euler's determinations may also be regarded with doubt in view of the use of an unstable substance such as ethylic acetate. The values deduced with the aid of carbon dioxide excite the suspicion that some carbonate may have been formed; the values obtained with thiocarbamide and salicylic acid are open to a similar criticism. In fact, few of the values to the right of the nitrous oxide column command confidence.

not hydrated. Taking the cases of sodium and potassium chlorides—which do not obey the dilution law either as regards freezing points or conductivity—and assuming that they are dissociated to about the same extent as caesium nitrate, Biltz calculates that the former can be associated with from 19–26 and the latter with 15–24 molecules of water, according to the concentration of the solution; these results are altogether different from those arrived at by Jones.

* 'Chem. Soc. Trans.,' 1907, vol. 91, p. 711.

† 'Mém. de l'Acad. de St. Petersb.,' 1875, vol. 22, p. 6.

‡ A lecture delivered to the Bristol Naturalists' Society, February, 1878, Chemical Society's Pamphlets.

§ 'Zeits. physik. Chem.,' 1900, vol. 33, p. 401.

|| *Ibid.*, 1897, vol. 24, p. 114.

The values in the other part of the table are both rational and in agreement with those given in the first column, except in the case of the ammonium salts, certain nitrates and the acids. An explanation has already been advanced of the low values obtained with the aid of methylic acetate in the case of certain chlorides and nitrates; to account for the irrational values given by the acids and in some cases by ammonium salts, it appears necessary to suppose that these exercise a specific solvent influence in presence of water. Setschenow has shown that carbon dioxide is about equally soluble in sulphuric acid and in water; the monohydrate $\text{H}_2\text{SO}_4 \cdot \text{H}_2\text{O}$, however, is a less effective solvent than either of its constituents separately and it is the mixture which has the minimum solvent power. This observation shows clearly both that acids can act as solvents of gases and that the association of water with another substance may lead to a diminution in its solvent power.

Taken as a whole, the outcome of the comparison of the values arrived at in various ways is very striking; it is certainly remarkable that it should be possible to deduce the degree of hydration of a salt from the diminution in solubility of a gas such as hydrogen, which dissolves only to the extent of 13 molecules per 1,000,000 molecules of water.

Such a result, taken in conjunction with the conclusions deduced from our hydrolytic studies, lends support to the view that solubility is to be regarded as a chemical phenomenon, as a manifestation of chemical affinity, even in the case of gases. If it be supposed that the gas molecules merely become interposed in the free spaces between the solvent molecules, it is to be expected that equal numbers of molecules would dissolve and that, within limits, the solubility would be independent of the nature of the gas. Again, if the molecular interspaces are limited in volume, some relation should obtain between the molecular volume of a gas and its solubility: gases of low molecular volume should dissolve the most readily. The facts do not fit in with either view* (Table II). The great difference in solubility between ethane, ethylene and acetylene, is especially remarkable, the solubility increasing to a marked extent in passing from the saturated paraffin hydrocarbon to the unsaturated olefine and to an altogether extraordinary extent in passing to the still less saturated acetylene.†

* Jahn ('Zeits. phys. Chem.,' 1895, vol. 18, p. 1) has suggested that the decrease in solubility should be proportional to the amount of surface covered by the solute. Drude and Nernst (*ibid.*, 1894, vol. 15, p. 79) consider that when ions are present the water is compressed by electrostriction.

† In this behaviour of the unsaturated hydrocarbons there is, perhaps, foreshadowed the altogether astonishing power possessed by charcoal—doubtless an ethenoid form of carbon—of absorbing gases at low temperatures which has been disclosed by Dewar's remarkable observations.

Table II.

Gas.	Molecular weight.	Solubility at 25°.	Molecules per 1,000,000 molecules of water.
		c.c. per litre.	
He	4	13.71	9.9
N ₂	28	14.32	10.3
H ₂	2	17.54	12.7
CO	28	21.42	15.5
O ₂	32	28.31	20.4
CH ₄	16	30.06	21.7
A	40	34.70	25.6
C ₂ H ₆	30	41.04	29.6
NO	30	42.23	30.5
N ₂ O	44	59.42	42.9
C ₂ H ₄	28	108.0	78.0
C ₂ H ₂	26	930.0	671.0

The solvent power of water for gases, etc., is modified by dissolved solids presumably in a variety of ways: (1) by the combination of water with the solute and the consequent diminution in the amount of free water; and (2) by the change in the equilibrium $(\text{H}_2\text{O})_n \rightleftharpoons n\text{H}_2\text{O}$ conditioned by the presence of the molecules of the solute, whether hydrated or unhydrated; the extent to which the gas is soluble in the dissolved substance or its hydrate is another influence to be taken into account; changes which the dissolved salt itself undergoes in its state of molecular aggregation in consequence of the interposition of the neutral molecules, when these are sufficiently numerous, will also affect the equilibrium. These various influences may come into play to counteract one another; consequently, the values obtained cannot be regarded as more than approximations.

The problem before us is to separate the cases in which there is minimum interference with the first-mentioned factor. Taking into account the low hydration values deducible from Knopp's determinations of the solubility of hydrogen in presence of potassium and ammonium nitrates, it appears that hydrogen cannot be used safely in all cases. The determination of the effect produced by neutral salts on the hydrolysis of cane sugar appears to be the most likely means of arriving at probable values—but even the values thus deduced must be regarded as minima, inasmuch as it must be supposed that the acid to some extent combines with the hydrolyte and that when the salt is added it may compete with the acid and alter the proportion of active acid as well as interfere mechanically with its action.*

It can scarcely be doubted that the forces at work in solutions are too

* Cf. IV, above.

complex in character to be expressed as simple mathematical laws. The fact that water is itself a complex material, which varies greatly in composition as the conditions are changed, has been left almost wholly, if not entirely, out of account in discussing electrolytic and hydration phenomena; and far too little attention has been paid also to the existence of salts in solution in various states of molecular aggregation.

The discovery of liquid crystals and the observations of Miers and his co-workers on the separation of solids from solution in the absence of nuclei capable of determining crystallisation, as well as the peculiarities manifest in saturated solutions such as are referred to in No. II of these studies, all afford indications of complexities which must not be omitted from consideration in dealing with solutions.

The average extent to which a salt becomes hydrated is obviously more or less dependent upon the amount of water available; this is clearly brought out in Table III, in which the values are given which may be deduced from various solutions of sodium chloride.

Table III.—Average Degree of Hydration of Sodium Chloride at various Concentrations.

Criterion.	Hydrolysis of cane sugar. (Caldwell.) 25°.	Solubility of nitrous oxide. (Roth.) 25°.	Solubility of hydrogen. (Steiner.) 15°.
5 normal	9.6	—	7.5
4 "	—	—	8.4
3 "	11	—	9.5
2 "	—	—	10.4
1 "	13	12	11.2
0.5 "	—	13.6	
0.25 "	—	17.4	

As the results obtained by the cane sugar method apply to weight-normal solutions and those obtained by the solubility method to volume-normal solutions, the values are not strictly comparable. The agreement appears to be closer when the results are expressed in terms of the number of molecules of free water present per equivalent of hydrate (Table IV); to obtain these values, it is assumed that the cane sugar and the chlorhydric acid appropriate between them $15\text{H}_2\text{O}$, leaving $\frac{1000}{18} - 15 = 40$ at the disposal of the salt. If the average hydration and the concomitant free water are expressed as co-ordinates, it becomes evident that the hydration value at infinite dilution will probably not exceed $20\text{H}_2\text{O}$.

Table IV.—Equilibrium between hydrated Sodium Chloride and free Water.

Sugar hydrolysis. (Caldwell.) Weight-normal solutions at 25°.	Solubility of hydrogen. (Steiner.) Volume-normal solutions at 15°.
5N..... NaCl 9·6H ₂ O ⇌ 8H ₂ O	5N..... NaCl 7·5H ₂ O ⇌ 2·9H ₂ O
3N..... NaCl 11·0H ₂ O ⇌ 13H ₂ O	4N..... NaCl 8·4H ₂ O ⇌ 4·7H ₂ O
N..... NaCl 13·0H ₂ O ⇌ 40H ₂ O	3N..... NaCl 9·5H ₂ O ⇌ 8·2H ₂ O
	2N..... NaCl 10·4H ₂ O ⇌ 16·5H ₂ O
	N..... NaCl 11·2H ₂ O ⇌ 43·4H ₂ O

Even the values in Table IV are not strictly comparable, as they refer to different temperatures. The influence of temperature is well brought out in Table V, deduced from Roth's observations on the solubility of nitrous oxide.

Table V.—Hydration of Sodium Chloride in volume-normal solution of gramme-molecular strength.

Temperature.	Hydration.
25	NaCl 12·0H ₂ O ⇌ 42·4H ₂ O
20	NaCl 12·3H ₂ O ⇌ 42·2H ₂ O
15	NaCl 12·6H ₂ O ⇌ 42·0H ₂ O
10	NaCl 13·3H ₂ O ⇌ 41·4H ₂ O
5	NaCl 13·9H ₂ O ⇌ 40·9H ₂ O

We believe that we are not justified in giving an absolute interpretation of any of the physical properties of solutions which involves the assumption that such properties are the outcome of the simple changes postulated by the advocates of the ionic dissociation hypothesis.

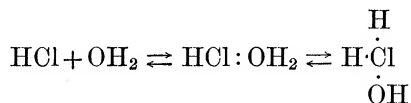
It is only when water is regarded as a changeable and ever changing substance that the full significance of the complex phenomena afforded by solutions becomes apparent. In future it will be necessary to pay more attention to the changes which the solvent itself undergoes and instead of thinking of interchanges as carried out in a mere space to contemplate their occurrence within a medium itself sensitive to every alteration occurring within it. It will be desirable, therefore, to abandon the use of solutions made up to particular volumes—except for analytical purposes—and always to use those instead which contain a known mass of solvent.

In discussing the phenomena of electrolytic conductivity in 1886,* the increase in molecular conductivity which attends dilution was attributed by

* 'Roy Soc. Proc.,' vol. 40, p. 268.

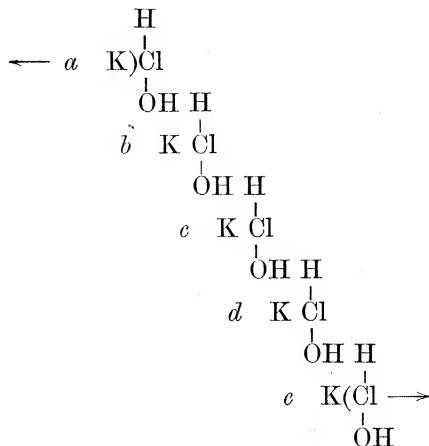
one of us to the gradual resolution of the more or less polymerised molecules of the salt into simple molecules or monads; conducting solutions were pictured as containing a *composite electrolyte* formed by the association of these monads with the solvent molecules; and the conclusion was formulated that "there is no satisfactory evidence that the constituents of the electrolyte are either free prior to the action of the electromotive force or are primarily set free by the effect produced by the electromotive force upon either member *separately* of the *composite* electrolyte but that an additional influence comes into play, viz., that of the one member of the composite electrolyte upon the other while both are under the influence of the electromotive force. This influence," it was imagined, "is exerted by the negative radicle of the one member of the composite electrolyte upon the negative radicle of the other member."

It is possible now to go somewhat further in explaining the process. The electrolytically effective monads must be thought of as hydrated in some particularly intimate manner, perhaps as hydroxylated, *e.g.*,



The proportion of the firmly hydrated or hydroxylated molecules in a solution of hydrogen chloride—which probably exists in solution, judging from its gaseous nature, entirely in a monadic form—will depend on the proportion of water present as well as on the affinity of the chloride for water and the correlated stability of the effective hydrate. From this point of view, the differences observed between salts in solution are conditioned both by the different extents to which they exist as polymerised molecules and as monads and by the different extents to which they exist as effectively hydrated monads; the underlying causes of these differences would be the different degrees of affinity inherent in the monads for one another and for water.

The process of electrolysis in a solution, say, of potassium chloride, may be pictured as involving a complete series of interactions among the hydroxylated monads polarised in a manner which may be represented diagrammatically thus:—



The attraction of the potassium and chlorine ions* to the electrodes may be supposed to determine an alteration of the "affinity" relationships within the molecules such as would permit, in the case of molecule *a*, of the hydrogen ion and the chlorine ion uniting if the OH ion attached to the chlorine ion at the same time were to become associated with the potassium ion of molecule *b*—and so on throughout the chain. The contiguous nascent molecules of hydrogen chloride and potassium hydroxide would interact forthwith. But the substances in solution would be hydrated beyond the hydroxide stage; and presumably both the hydrogen chloride and the potassium hydroxide would attract more water immediately they were formed. Probably in the rearrangement water would be carried in both directions but in different amounts corresponding to the different degrees of hydration of the two compounds. The mobilities of the "ions" would be more or less affected by and dependent on the extent to which the compounds were hydrated.

* I have more than once pointed out that the modern use of the term ion—and of its correlative ionisation—is not such as was contemplated by Faraday. It is desirable that some agreement were arrived at and that the conception of dissociation were separated implicitly from both terms. Words are never idle used wrongly, they give rise to false impressions:—"through a very imperceptible but still very dangerous, because continual influence, they do great injury to science by contracting and limiting the habitual views of those pursuing it" (Faraday); "those who are not familiar with a subject are very liable to be misled by the deceptive appearance of simplicity conferred by particular names" (FitzGerald). There are now three partially synonymous terms in use, each of which has its special value—the first is atom, the second radicle, and the third ion. The term atom, of course, applies to the elementary, undivided unit; the term radicle is of more general use, being applicable both to atoms and to groups of atoms which can function as atoms; both these terms have only a structural significance. The ion, however, is the movable, transferable radicle; a radicle may be said to be an ion and to be ionised to a particular extent, if it be movable by chemical means to the particular extent to which it is said to be ionised.—H. E. A.

Although the water is thought of as attached only to the negative ion, both ions would appear to be hydrated, on this hypothesis.

The arrangement suggested is but a modification of the Grotthus' chain. It is difficult to avoid the conclusion that the facts on the chemical side are such as require some such explanation of the phenomena, and that we are justified in asking physicists to re-examine the arguments which have led them to take exception to the Grotthus explanation. FitzGerald has already spoken with no uncertain voice and given us his support, in his memorial lecture on Helmholtz. Of late years probably no one has shown greater power of appreciating all sides of the position: his adverse criticism of the dissociation hypothesis is therefore of peculiar value.

The Effect of Pressure upon Arc Spectra. No. I.—*Iron.*

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(Abstract.)

The first part of the paper contains a description of the mounting and adjustment of the large Rowland Concave Grating in the Physical Laboratory of the Manchester University. The feature of this is the stability of the carriages carrying the grating and camera, and the novel construction and attachment of the cross-beam, which secure the absence of any disturbance which might be caused by bending or sagging.

The second part describes experiments made with a pressure cylinder designed by Mr. J. E. Petavel, F.R.S., in which an arc is formed between metal poles opposite a glass window, through which the light is examined by means of the Grating Spectroscope. A system of mirrors allows the image of the arc, however unsteady it may be, to be kept almost continuously in focus upon the slit.

Two sets of photographs of the iron arc in air have been taken for pressures ranging from 1 to 101 atmospheres (absolute), and the results are given below for wave-lengths $\lambda = 4000 \text{ \AA.U.}$ to $\lambda = 4500 \text{ \AA.U.}$

I. *Broadening.*

1. With increase of pressure all lines become broader.
2. The amount of broadening is different for different lines, some almost